Supramolecular effects in self-assembled monolayers: general discussion

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(1:[1]1) Steven Tait opened the discussion of the introductory lecture by Rasmita Raval: You made an analogy in your presentation between polymorphism and the many chemical functions that happen in parallel in a cell. In studies of molecular self-assemblies, there is o□en a tendency to look for a single low energy structure that could potentially have a distinct, single chemical function. Do we need to reconsider this mindset in order to take advantage of potential bene□ts of polymorphic systems that could potentially be developed as multi-functional systems? What suggestions do you have for designing and characterizing polymorphic molecular systems that have useful multi-functionality?

Rasmita Raval replied: Polymorphism is o□en ignored entirely, as most researchers continue to concentrate on solving a de□ned phase. I feel strongly that polymorphism is a fantastic attribute that complex molecules display at surfaces. Each phase will have its unique chemical and geometric structure, with a distinct functionality. Therefore, one now has the possibility to create many functions from a single molecule-single surface system, simply by changing conditions such as coverage, temperature, pH, etc. which lead to different thermodynamically preferred assemblies, or via kinetic capture of metastable states.

Natural systems use such attributes to create highly responsive systems, or to switch certain functions on and off. We should be prepared to 'roam' across the phase-space, map the phases that are created and, most importantly, explore the functions that each phase could deliver. Such information is the basis for exploiting polymorphism to create smart surface systems that harness the □exibility of the system and display different functions by design. One can imagine that such approaches can then be extended by creating local environments which favour speci□c phases, thus providing a route towards a system that concurrently displays multiple functions in local domains across a surface. One could take this further whereby the function of one domain acts as impulse or feedback for a neighbouring domain, creating a communicating multifunctional surface, which would be a 2D mimic of the multifunctional cell.

(2:[2]2) Talat Rahman commented: You've raised a number of interesting issues; one which somehow we've not yet taken into account is entropic effects. When you were showing the slide with the arrangements of your enantiomers, differences in their energies were of the order of tens or hundreds of millivolts, which is about where entropic contributions can be expected to play a role. The other thing, which we're □nding now, and your disordered systems allude to that, is the issue with adsorption sites. We typically consider those that are the most obvious. Yet recent □ndings using machine learning, for example, reveal possible adsorption sites that one may not assume naturally. On second thought they make sense, because most of the time adsorption is determined by the nature of the orbitals in the bonding layer. Would you agree then that the disorder seen in your experiments may be related to the system having to choose amongst a number of adsorption sites with similar binding energies?

Rasmita Raval answered: Entropic effects are largely ignored at present, since they are difficult to measure experimentally in surface systems, and difficult to calculate. You are absolutely right to point out that the enthalpic energies calculated for different phases o□en vary by very small amounts. Therefore, entropic factors will play a key role in determining which phase is exhibited at a particular temperature. This also increases the polymorphism of a system and, with it, the opportunities to design system function as I have outlined in my reply to the previous question from Steven Tait. Our work has also shown that entropy plays a critical role in determining both the disordered and ordered phases at a surface.[1] In the case we studied, entropic effects determined the ordering propensity of each enantiomer. Your second point on adsorption sites is also important. Given the complexity of the molecule–surface system, there is a tendency to iterate calculations around obvious adsorption con□gurations. However, you are right that different adsorption sites o□en differ by small energy differences and your suggestion of using machine learning to fully sample the parameter space to capture the variety of con□gurations available to a single adsorbed species is a good way forward. In addition, we need to recognise that the relative energies for the different adsorption con□gurations can change signi□-cantly when translating from the single adsorbed molecule to the organised phase. Therefore, there is also a need to explore all the permutations that could occur in the ordered phase. We certainly saw the importance of this when we revisited the tartaric acid/Cu(110) system (as described in my lecture and in ref. 2). Finally, does the disordered phase include a number of different adsorption con□gurations that are close in energy? This is difficult to prove experimentally except in large molecular systems where each adsorbate could potentially be mapped. Clearly, there will be a Boltzmann distribution of different species within the disordered phase and entropic factors will become important for such systems. Undoubtedly, a fascinating area of discovery for the □eld of complex molecules at surfaces!

1 S. Haq, N. Liu, V. Humblot, A. P. J. Jansen and R. Raval, Nat. Chem., 2009, 1, 409.
2 G. R. Darling, M. Forster, C. Lin, N. Liu, R. Raval and A. Hodgson, Phys. Chem. Chem. Phys., 2017, 19, 7617.

(3:[3]3) Karl-Heinz Ernst asked: Rasmita, you mentioned that one has to take all options into account when resolving the structure of an adsorbate or a selfassembled domain, e.g. the Cu(110)/TA-(9 0, 12) phase. How about surface reconstruction or Cu adatoms? Shouldn't these options be taken into account as well?

Rasmita Raval replied: You are absolutely right. The response of the surface to the molecule is a critical factor. We had demonstrated molecule-induced surface reconstruction back in 1990 when we showed that the CO molecules could reconstruct the Pd(110) surface once a critical coverage had been reached.[1] Even more surprising was the fact that as the coverage is increased, the reconstruction is li□ed and a new surface assembly is created. This system certainly showed not only that surface reconstruction should be considered, but also that the reconstruction can be surface phase-dependent and can be induced and li□ed during the course of adsorption and assembly. We certainly considered the possibility of surface reconstruction for the Cu(110)/TA-(9 0, 12) phase, especially given the strength of chemisorption of the bitartrate to the surface. However, so far, our experimental or theoretical data do not indicate any drastic reconstruction.

1 R. Raval, S. Haq, M. A. Harrison, G. Blyholder and D. A. King, Chem. Phys. Lett., 1990, 167, 391–398.

(4:[4]4) Claire-Marie Pradier said: With your molecular assemblies and supramolecular systems, you're very close to the molecular machines (Nobel prize this year). To go further, could molecules which have the same functions together display coherent motions on the surface? Please could you comment on that?

Rasmita Raval replied: Yes, indeed, the 2016 Nobel Prize in Chemistry has been really inspirational! For many future technologies, we will require molecular machines at surfaces. Here, we are going to have to combine a number of aspects e.g. the motion of single molecular entities, the creation of supramolecular or covalent architectures that con□ne or direct the motion, the ability to switch systems, creating recognition sites for docking, etc. Furthermore, all of this will need to be achievable at operable temperatures, e.g. room temperature. Our paper[1] describes a simple surface system that we created in collaboration with David Amabilino and Lluisa P´erez-Garc´ıa, where a simple walker molecule walks along a particular surface track, with the motion con□ned by covalent porphyrin

fences created by on-surface synthesis. One can say that this system has analogies to the rotaxane molecule where travel of the macrocycle ring occurs along a de□ned track and is con□ned by two end stations. A particular aspect of our work is that the walker molecule chemisorbs to the surface via two 'feet', which then detach and attach in an inchworm fashion as shown by the calculations undertaken by Lev Kantorovitch's group. This strong interaction means the system can operate at room temperature. This is just the □rst step – we now need to design systems that will actually perform work!

1 S. Haq et al., Angew. Chem. Int. Ed., 2015, 54, 7101.

(5:[5]5) Manfred Buck enquired: You presented an example of onedimensional motion of molecules between barriers and, in this context, molecular machines were mentioned. Since, for the system presented, the motion is a random walk in 1D, are there any ideas/concepts apart from scanning probebased ones which might lead to a directed motion?

Rasmita Raval responded: You are right, the simple surface molecular machine system I discussed shows 1D directional motion, but with random stochastic steps in either direction. Tip-induced directed motion has been demonstrated for surface species. Away from scanning probe-based solutions, one will have to use approaches such as using functional groups that can be activated e.g. by light, pH or redox cycles, incorporating catalytic centres that provide fuel, designing in asymmetry or Brownian motion ratchet approaches used in natural systems, utilising chemical gradients, anisotropic physical □elds and non-equilibrium systems that direct motion. What is clear is that there is plenty of science that remains to be tackled!

(6:[6]6) Steven De Feyter asked: Probably a more philosophical question: to what extent are we biased by the things that we can "see" using our techniques? To what extent do we really grasp reality if we are biased to look at "static features" rather than "dynamic systems" because of the limitations of the instrumentation or methodology that we use?

Rasmita Raval responded: A truly philosophical question for all science! We construct our scienti□c knowledge on measurable things and are largely blind to that which is unmeasurable. As our techniques advance, our knowledge base comes under scrutiny (the evolution of quantum mechanics is a □ne example). However, it is true that order, symmetry and static structures are o□en given the greatest attention in many great □elds of science. I am convinced that we need to re-balance our perspectives and to actively seek disorder, non-equilibrium and transient aspects in our □eld. This will need both a change in scienti□c attitude (by scientists, editors and the funding authorities!) and the development of better spatial- and time-resolved techniques and theory.

(7:[7]7) David Amabilino commented: A really interesting point was raised about disorder in supramolecular structure in layers being ignored sometimes. If you look at "disorder" from a covalent chemistry perspective being the formation of non-desired molecules, when synthesis is performed in solution we might get a 60% yield, so 60% is what you wanted, what was the rest? That 40% goes mainly unidenti□ed. This is a great opportunity for surface science to try and understand and direct chemistry, where techniques could be eventually used to identify each product on a surface and control reaction pathways through concentrations and temperature. How far away in time do you see this dream coming true?

Rasmita Raval answered: You raise a really important and interesting point here. In this context, one can deploy the local analytical techniques that are now at the disposal of a surface scientist and observe model covalent reactions at a surface and identify the variety of products created, even quantify the ratios. Now that on-surface covalent organic synthesis has become part of our repertoire, it would be interesting to undertake test reactions and address this question directly. Speci□cally, it would be instructive to expand our observations from products we want to see, to the others that demonstrate the diversity of outputs, including messy, disordered products. As you state, the opportunity exists to alter reaction conditions and observe their effect on product distribution, with the prize of delivering the parameters that guide reactions. How far away are we from this dream? Well, I think we are actually ready to start straightaway on surfaces! We will need to create close conversations between organic chemistry, surface science and theory to design systems that will allow us to observe, learn and then engineer outputs. Will this throw light on organic synthesis in solution? Maybe not directly, but I have no doubt that generic principles will arise that can be translated. Finally, I also point out that the recent advances in local probing at

surfaces means that the time is ripe to re-visit heterogeneous catalysis and address the central questions of activity and selectivity in surface reactions.
(8:[8]8) Talat Rahman noted: Just a quick comment about the interpretation of experimental data; looking at scan images, the tip is playing a major role there, and it has to be included in nucleation. We are seeing what is happening, but our interpretation is not there yet.
Rasmita Raval answered: Tip effects are, of course, known to be important in imaging and progress is being made on modeling different types of tips. We also know that in some systems, the tip appears to be actively involved in nucleating an island, or dispersing an existing island. There is little understanding or interpretation of exactly what is happening here. It would be interesting to understand this phenomenon. Perhaps we could then exploit it to nucleate and write organised molecular structures where we wanted them.
(9:[9]9) Talat Rahman opened a general discussion of the paper by Ioan Bˆaldea: Your results are sensitive to the coverage of the molecule. Did you perform the calculations for several coverages? Also, van der Waals interactions are expected to be important, both for molecule–surface and inter-molecular interactions. Did you try out different ways of incorporating these interactions?
Ioan Bˆaldea replied: Thanks for your two-fold question. To your □rst point: yes, I performed calculations for more coverages than I've shown in the paper. The (6 _ 6) arrangement is shown as a typical case of very low coverage. Increasing the coverage by a factor of 6 in a (3 _ 2) arrangement – which corresponds to the unit cell of the herringbone ordering wherein one out of the two molecules is removed – yields no notable change in the twisting angle, the value of which is basically that of isolated molecules. The problemwith variable coverages is that the coverage cannot be varied continuously; so, one cannot investigate whether the increase in twisting angles from _36_ to _76_ is abrupt or gradual. Varying the coverage (quasi) continuously amounts to investigating incommensurate SAM superstructures, situations that can be mimicked only by choosing very large SAM unit cells, which are computationally prohibitive. To the second point: I show in the paper results for SAMs adsorbed in Au(111) demonstrating that van der Waals corrections are not quantitatively signi□cant: please compare the results of the "standard" calculations without dispersion corrections (acronym "0.02") with those obtained by including dispersion corrections (labeled "VDW-DRSLL") in Tables S6 and S7 of the ESI. To this aspect I must still note that several earlier works on some SAMs adsorbed via thiol groups already found that dispersion corrections are negligible.
(10:[10]10) James Batteas remarked: Could you comment on the energy barrier for the rotation in this system? You've isolated these two main states, but there will always be some □uctuations due to thermal effects. Could you comment on any relative impacts from thermal motions here on the transport?
Ioan Bˆaldea answered: Thank you, this is certainly a relevant aspect. Unfortunately, the state-of-the-art of the theory does not allow accurate values of the torsional energy barrier to be achieved. Even the torsional energy barrier of the isolated biphenyl molecule (amounting to _0.1 eV according to experiments[1]) could hardly be reproduced theoretically;[2] quantum chemical calculations at such elaborate levels[2] for molecules forming SAMs adsorbed on metals are hopeless at present. Nevertheless, values of _0.1 eV are still four times larger than the thermal energy at room temperature, and for this reason it is hard to imagine that, albeit signi□cant, thermal □uctuations would completely wash out the impact of torsional angle on conductance. In fact, due to steric hindrance I would expect higher torsional energy barriers for molecules densely packed in SAMs than for isolated molecules. In addition to this, for studies on the related bipyridine molecule[3,4] it is known that the torsional motion is highly anharmonic. To compute currents, ensemble averaging over the various molecular conformations has to be performed,[5,6] and this anharmonicity acts to suppress □uctuations away from the averaged value of the torsional angle.
1 O. Bastiansen and S. Samdal, J. Mol. Struct., 1985, 128, 115.
2 M. P. Johansson and J. Olsen, J. Chem. Theor. Comp., 2008, 4, 1460.
3 I. Bˆaldea, EPL, 2012, 99, 47002.
4 I. Bˆaldea, J. Phys. Chem. C, 2014, 118, 8676.
5 I. G. Medvedev, Electrochim. Acta, 2008, 53, 6545.
6 I. Bˆaldea, J. Phys. Chem. C, 2013, 117, 25798.
(11:[11]11) Trolle Linderoth enquired: What is the energy difference between the two conformational states? For instance, in your condensed, herringbone layer of molecules where you have a preferred intramolecular angle of 76_ between the two benzene rings, what would happen if as a defect you introduced a molecule

with the 36_ angle preferred for the isolated molecules? Information on the energetics would allow to estimate to what extent these states are populated in the experimental situation at room temperature.
Ioan Bˆaldea answered: Thanks for your interesting question. The unit cell used in calculations for SAMs of BPMT and BPDT with herringbone arrangement has 62 atoms and 64 atoms, respectively. To simulate a concentration of defects amounting to 1/9 (so, a pretty high value), given the fact that SIESTA employs periodic boundary conditions, one would need unit cells containing at least 3 _ 3 _ 62 ¼ 558 and 3 _ 3 _ 64 ¼ 576 atoms for BPMT- and BPDT-based SAMs, respectively. With computational resources available to date, such calculations for any theoretical approach that could be trusted. One could expect that the energy to create such a defect is something of the order of the torsional energy barrier of isolated biphenyl (_0.1 eV, cf. ref. 1). For elaborate ab initio theoretical approaches it was already a big challenge to reproduce the experimental value for this case (one isolated biphenyl molecule!). Johansson and Olsen[2] drew attention to the fact that using basis sets of at least augmented quadruple zeta quality is a crucial prerequisite. To reach the accuracy of ab initio methods, hybrid exchange–correlation functionals (B3LYP) are needed in DFT calculations, which – parenthetically – are not implemented in SIESTA. Concerning the temperature effect: albeit not extraordinary large, energy barriers of _0.1 eV (in fact, for molecules forming SAMs adsorbed on electrodes I would expect more than for isolated molecules) are still signi□cantly larger than the thermal energy of _26 meV at room temperature. Therefore, although thermal uctuations can be signi□cant, it is hard to believe that the effect will be wiped out.
1 O. Bastiansen and S. Samdal, J. Mol. Struct., 1985, 128, 115.
2 M. P. Johansson and J. Olsen, J. Chem. Theor. Comp., 2008, 4, 1460.
(12:[12]12) Robert Jones asked: In the paper you refer to a herringbone surface structure, e.g. in Fig. 2 and associated text. Clean Au(111) undergoes a herringbone reconstruction. It is unclear to me whether the substrate gold (111) surface has the herringbone reconstruction, or whether it is the SAM that has the herringbone structure on top of a bulk terminated Au(111) surface. Could you clarify this please?
Ioan Bˆaldea responded: Thanks for your interesting question. In the “standard” calculations (acronym “0.02”) I took gold layers of fcc Au(111) with gold–gold separation frozen at the experimental value d ¼ 2.88367 °A. The twisting angles obtained in this way do not notably differ from the values obtained by also optimizing the positions of the gold atoms in the top layers (acronyms “CAB-R” and “CABCAB-R”); compare the $4_{1,2}$ values of the second line with those of the last two lines in Tables S6 and S7 of the ESI (DOI: 10.1039/C7FD00101K).
(13:[13]13) Manfred Buck commented: For thiol layers, the binding of the head group to the substrate exerts a decisive in□uence on the structure of the SAM. In addition, the Au surface signi□cantly restructures upon SAM formation which also involves Au adatoms. Has the in□uence of the interface structure on the SAM structure been looked at, i.e., have unreconstructed and adatom-containing models been compared?
Ioan Bˆaldea replied: The results of my calculations – whether without or with reconstruction, in cases where I included it (cf. the last two lines in Tables S6 and S7 of the ESI, DOI: 10.1039/C7FD00101K) – support the prevailing view that adsorption occurs at hollow positions. Still, to reiterate what I said in the paper, results on the preferential adsorption position of both experimental and theoretical studies published so far are controversial.
(15:[15]15) Trolle Linderoth remarked: Your conclusion seems to be that the key effect of two conformational states is rather independent of the details of the interactions to the gold substrate; could the important effects be modelled in a 2D system without the substrate, and perhaps thereby allow the intermolecular distance to be varied continuously?
Ioan Bˆaldea replied: This is a very interesting question. Work done in this direction since I submitted the manuscript is encouraging. A two-dimensional model seems to be able to capture the essential aspects of the interactions, allowing at the same time a continuous variation of the intermolecular spacing.
(16:[16]16) Manfred Buck said: In the SAM calculations, does the torsion angle between the aromatic rings of biphenyl depend on the starting conditions? Is there a difference in the □nal SAM structure if the calculations start from a signi□cantly twisted conformation of the biphenyl as found in an isolated

molecule or a coplanar conformation?
Ioan Bˆaldea replied: Thanks for raising an interesting point. Occasionally, starting with twisting angles very different from the most stable con□guration (e.g., near coplanarity), I found situations where optimization ended with con□gurations wherein one molecule had a torsional angle of _40_ and was substantially tilted (tilt angle q _ 40–50_ with the normal to the electrode surface), while the second molecule (I am referring to the herringbone unit cell) had a twisting angle 4 _ 76_, and stood nearly upright on the metal surface. However, such con□gurations (metastable or transition states?) were by a few tenth of eV higher in energy than the lowest energy extremum (corresponding to $4_{1,2}$ _ 76_ and nearly "vertical" molecules), which was recovered by slightly perturbing that starting conformation.
(18:[18]18) Rasmita Raval opened the discussion of the paper by Pol Besenius: You have shown beautiful supramolecular assemblies for your system. O□en, such assemblies are probed by techniques such as CD that give the average response of the system. However, it would seem that most of the structural models are derived from molecular dynamic calculations. What experimental methods are currently being applied to such systems to get independent veri□-cation of structure, or is this currently too challenging?
Pol Besenius replied: We used sum frequency generation and IR vibrational spectroscopy experiments to show that the structures are ordered in our □rst report on these sequentially-grown copolymers.[1] SFG experiments suggested that the degree of order increased with the number of added monomers. In IR spectra of the surface-gra□ed copolymers the amide I and II bands were characteristic for hydrogen-bonded secondary structures, which were similar to a material that was self-assembled in solution and then deposited on a Au surface. Typically, in solution studies of the copolymers, we perform CD, WAXS, FRET, as well as TEM, cryoTEM and PFG-NMR.[2−4]
1 H. Frisch et al., Angew. Chem. Int. Ed., 2016, 55, 7242–7246.
2 R. Appel et al., Chem. Eur. J., 2015, 21, 19257–19264.
3 H. Frisch et al., Chem. Eur. J., 2015, 21, 3304–3309.
4 H. Frisch et al., Angew. Chem. Int. Ed., 2013, 52, 10097–10101.
(20:[20]20) Trolle Linderoth asked: The state of your monomer, is that known? Should we think of that as 2D □at or globular, and how does this affect the selfassembly on the surface?
Pol Besenius replied: We have previously shown with TEM that the monomers □atten out on a surface.[1] A manuscript has just been submitted where we looked at the copolymer formation in solution with multi-angle dynamic light scattering. In isolated solutions of physiological ionic strength, both monomers have a hydrodynamic radius of 1.9 nm and are globular. However, from unpublished work, we know that the dendritic core is important. If it is too □oppy, the growth into anisotropic nanorod-like objects is not favourable.
1 H. Frisch et al., Chem. Eur. J., 2015, 21, 3304–3309.
(21:[21]21) Claire-Marie Pradier commented: You mentioned in the title surface-con□ned supramolecular copolymers. In fact, you build con□ned surface polymers because you bind them to initial layers with a density that is controlled by yourself; why is such a control of the multilayer density (con□nement at the surface) so important?
Pol Besenius responded: The sequential growth of copolymers occurs on the surface-bound layers. In that sense we manage to con□ne the assembly on the surface, and solution self-assembly is avoided. I agree, we do not describe a selfassembly process between two states that are both bound or con□ned on the surface, but we use the surface as a means to con□ne the copolymer growth. The density of the initial layer is critical. If it is not high enough, the rods that grow off the surface start to collapse or □atten out on the surface.
(22:[22]22) Trolle Linderoth said: To help clarify the question I think all the surface scientists in the audience have in mind: your cartoons show distinct columns of alternating molecules. Is there such a degree of 2D order, or should we think of your structures as alternating disordered layers?
Pol Besenius replied: In our □rst report on these sequentially-grown copolymers, we used sum frequency generation and IR vibrational spectroscopy experiments to show that the structures are ordered.[1] SFG data suggested that the degree of order increased with the number of added monomers or molecular layers. In IR spectra of the surface-gra□ed copolymers the amide I and II bands

were characteristic for hydrogen-bonded secondary structures. These were similar to a material that was self-assembled in solution and then deposited on a Au surface.

1 H. Frisch et al., Angew. Chem. Int. Ed., 2016, 55, 7242–7246.

(23:[23]23) Sebastian Schwaminger commented: I have a question concerning the QCM measurement. You assigned the viscoelastic effects to a so□ polymer. Is it possible that the viscoelastic effect at 45 _C, or at least part of this behaviour, is caused by temperature effects? Or is this effect dependent on the copolymer structure exclusively?

Pol Besenius replied: The experimental data obtained from temperature- and solvent-dependent SPR experiments combined with the QCM-D studies suggest that at higher temperatures more monomer molecules are adsorbed on the surface, which leads to a thicker and so□er polymer matrix, compared to the ones at low temperatures. You are right, though, in suggesting that temperature effects in the viscoelastic properties of the polymer □lm cannot be excluded.

(24:[24]24) Amar Flood said: A very nice talk. I need some clari□cation on the data recorded at room temperature relative to higher temperatures, as shown in Fig. 2 of your paper (DOI: 10.1039/C7FD00100B). It seems that you get a greater SPR response at higher temperatures. Is this because more material is going down in a layer-by-layer manner at higher temperature? I would assume yes. However, as I understand layer-by-layer, you always need equal charge balance to achieve regular steps with each layer, just as you observed. So, do you know why more material needs to go down at higher temperature to balance the charge than at lower temperatures?

Pol Besenius replied: This is a good point. I agree with your interpretation of the temperature-dependent SPR data. The differences in the incremental increase in the SPR signal (Fig. 3 of the paper, DOI: 10.1039/C7FD00100B) suggest nonlinear temperature-dependent behaviour, which is indicative of desolvation of the triethylene glycol shell of the copolymers. As you suggest, charges must be neutralised a□er each sequential monomer addition to avoid accumulation which would inhibit structure formation. However, in our sample preparation we make sure that for all temperatures we start the kinetic measurements with the same □rst dense layer of cationic monomers, thus a surface that is saturated as pointed out in the experimental part. We therefore assume that the structure formation is more efficient at higher temperatures, due to a combination of lower steric demand of the desolvated dendritic triethylene glycol chains and the more pronounced entropic contribution originating from the counterion release upon electrostatic binding. The data in Fig. 4 of the paper support this notion, since the addition of acetonitrile suppresses thermoresponsive behaviour of the side chains. Indeed, the difference in the SPR data at 25 _C and 45 _C becomes very small a□er the addition of 20 vol% acetonitrile to the aqueous buffer.

(27:[27]27) Yuri Diaz Fernandez commented: Regarding the remarkable temperature dependence observed in your system for both SPR and QCM data, how will the exchange of dendritic molecules adsorbed in the □rst layer affect the subsequent growing of the multilayers? Expecting an increase in the exchange rate with temperature, could the formation of mixed layers explain the increase in mass per single functionalisation step observed at higher temperatures?

Pol Besenius responded: Since in the current system every monomer has six thioether groups, and could displace the surface-bound oligomers or polymers, I would expect that higher temperatures and an increase in the exchange dynamics would decrease the driving force for the formation of supramolecular multilayers. This is not supported by the experimental data. We have therefore assigned the temperature-dependency to the LCST behaviour and desolvation effects of the dendritic ethylene glycol chains. We have shown that the addition of 20% acetonitrile to the aqueous comonomer solutions supports this notion, since the LCST effect vanishes and the temperature-dependency is much less pronounced.

(29:[29]29) Han Zuilhof said: Your idea of a one-on-one ordered structure based on the SPR data hinges on the refractive indices. Given the sizes of these molecules (identical, but for one small functional group), it is likely that the refractive indices are nearly equal. However, the additions of compounds 1 and 2 are really not equal (especially in Fig. 4 of your paper, DOI: 10.1039/C7FD00100B, is this clearly observable); what are your opinions about the refractive indices of these materials, and do you have evidence to suggest that it must indeed be the difference in refractive indices, rather than a loss of order, that must cause this effect?

Pol Besenius responded: I agree, the differences in the incremental refractive index changes for the anionic compared to the cationic monomer are surprising. This observation cannot be explained just by the small difference in molecular weight of both species. Your point about the difference in supramolecular order caused by the addition of the monomer is valid. In our initial report,[1] the SFG data suggested that the order increases with the layer thickness. Intriguingly, when focussing on the C]O signal of the glutamic acid side chain modes, we observed an increase even a□er the addition of the lysine-containing comonomer. This suggests that the order of the surface-bound stacks is dictated by interactions between both monomers and that the order within the stack, or at least in the active chain end, changes a□er the addition of each species.

1 H. Frisch et al., Angew. Chem. Int. Ed., 2016, 55, 7242–7246.

(30:[30]30) Han Zuilhof asked: Relating to that one-on-one order you refer to, could you see in IR measurements hydrogen bonding on your surface as you have in solution? And do you have AFM data that would indicate the step-by-step growth of the thickness, rather than only for an extended series of alternations?

Pol Besenius responded: As I mentioned, we used IR spectroscopy to show that the structures are ordered.[1] In the IR spectra of the surface-bound copolymers, the amide I and II bands were characteristic for hydrogen-bonded secondary structures. These were similar compared to a material that was self-assembled in solution and then deposited on a Au surface. With respect to the AFM data, in that same paper we performed experiments for a sequential number (n) of monomer addition steps (n ¼ 10, 20, 30) and looked at the change in the height pro□les. From a linear regression we estimated an increase of 0.68_0.05 nm per monomer. So far, we have not performed AFM characterisation in smaller incremental steps.

1 H. Frisch et al., Angew. Chem. Int. Ed., 2016, 55, 7242–7246.

(31:[31]31) Steven De Feyter enquired: Could you explain to what extent your approach is different from what is known as electrostatic self-assembly, or layer-by-layer assembly of polyelectrolytes? What is different, if so, in your approach and outcome?

Pol Besenius replied: I agree, our strategy resembles the well-known layer-bylayer self-assembly of oppositely charged polyelectrolytes into multilayered □lms. However, using b-sheet encoded amphoteric peptides, a combination of hydrogen bonding and hydrophobic shielding, in addition to the Coulomb attractive interactions, allow us to tune and control the produced architectures at multiple levels. This is not easily achieved for the non-directional layer-by-layer deposition of charged polymers. I particularly emphasise that the chiral bsheets direct the self-assembly perpendicular to the Au surface, and the number of monomer addition steps de□nes the height of the copolymer and resolution is achieved on a sub-nanometer level. Both of these factors will be important in the optoelectronic applications we are currently pursuing.

(32:[32]32) Karl-Heinz Ernst opened a general discussion of the paper by Vincent Humblot: In your talk and in many other papers, zwitterionic states of amino acids are reported. I followed this for many years, and from what I've seen, especially on gold surfaces, this could be questionable. Many people work with the N 1s XPS peak at roughly 402 eV and assign them to NH_3^+ (or equivalent if secondary or tertiary amino groups). But I've seen papers where people adsorb nitrogen-containing compounds on gold, where we see this peak and there's no way that we have any acidity such that protonation of the nitrogen can occur. Gold is the metal with the highest electronegativity and may be the acceptor for the lone pair from the nitrogen. Shouldn't we discuss, at least for nitrogen-containing compounds on gold, other possibilities than zwitterions? I think we have to be careful about assigning a number of 402 eV to zwitterionic states.

Vincent Humblot responded: This is quite a good and a tricky question all together. We agree that a peak around 402 eV has been observed for molecules that cannot have a positively-charged nitrogen such as quinolone and cinchonidine adsorbed on Au(111) surfaces.[1] However, these molecules are quite different from amino acids and small peptides due to their peculiar structure and the presence of unsaturated benzene rings. In the cases of amino acids, and more precisely in our Gly–Pro case, there is no presence of such conjugated systems due to aromatic compounds. In addition, our assignment of the high-energy peak at 402 eV is not made blindly and is supported by literature results (see for instance reviews ref. 2 or ref. 3), and by comparing the several peaks that we can obtain for our molecules. We, for instance, take great care at looking at the energy differences,

especially the splitting between the NH amide group and the second peak at higher energy with a difference of 1.4 to 1.7 eV following adsorption of GP on Au(110), with a peak at 400.2 eV for NH, NH_2 and another one at 401.6 eV for NH_3^+ species. Another example lies with the adsorption of Gly–Pro on a Cu(110) surface under two very interesting chemical forms: anionic (top panel of Fig. 1) and zwitterionic (bottom panel of Fig. 1).[4] In that example, one can clearly see the splitting of the nitrogen N 1s peak with a second component at higher energy arising for the zwitterionic adsorbed molecule at an energy higher by 0.8 eV, centred at 401.1 eV. Finally, I would like to cite three more examples where the same molecule (methionine) was adsorbed as zwitterionic or anionic species on three very different surfaces: Cu, Ag and Au. For Cu(111), anionic species gave a single peak at 399.5 eV with a second one at 401.3 eV for the zwitterionic molecules,[5] while on Cu(110) anionic molecules exhibited a single peak at 400.1 eV.[6] On Ag(111), methionine adsorbed as zwitterions and presented a single N 1s peak at 401.15 eV,[7] and its equivalent study on zwitterions on methionine/Au(111) ended up also with a single peak at 401.6 eV.[8] To conclude, taking into account all these examples we can fairly assume, even con□rm, that in the present case, the peak observed at high binding energy (401.6 eV) following adsorption of Gly–Pro/Au(111) is unambiguously assigned to NH_3^+ species.

1 B. Behzadi et al., Appl. Surf. Sci., 2007, 253, 3480–3484.
2 K.-H. Ernst, Phys. Status Solidi B, 2012, 249, 2057–2088.
3 S. M. Barlow and R. Raval, Surface Science Reports, 2003, 50, 201–341.
4 C. M´ethivier et al., J. Phys. Chem. C, 2016, 120, 27364–27368.
5 A. Schiffrin et al., J. Phys. Chem. C, 2009, 113, 12101–12108.
6 C. M´ethivier et al., Surf. Sci., 2015, 632, 88–92.
7 A. Schiffrin et al., PNAS, 2007, 104, 5279–5284.
8 V. Humblot et al., Langmuir, 2014, 30, 203–212.

(33:[33]33) Karl-Heinz Ernst asked: In your RAIR spectra, how unambiguous is your assignment of vibrations of a NH_3^+ group?

Vincent Humblot responded: We agree that our PM-RAIR spectra could be ambiguous to analyse for two main reasons: the low intensity of the signal (small surface and very thin □lm) and the multiplicity of vibrations in the 1500–1700 cm_{-1} region. However, by doing cross-checking in between the different IR data we have obtained for Gly–Pro adsorbed on Cu(110) as anionic and zwitterionic molecules[1] or our very recent results on the adsorption of glutamic acid on Cu(110) [2] and the literature available on several amino acids adsorbed on coinage metals, we can be fairly con□dent with our assignments of the IR data. Nevertheless, one can never be 100% sure of these assignments, especially when in a 100 cm_{-1} region, one can □nd so many vibrational bands: NH_3^+ and NH_2 deformation mode, COO_- stretching mode, amide I and II bands (in the case of peptide).

1 C. M´ethivier et al., J. Phys. Chem. C, 2016, 120, 27364–27368.
2 R. Totani et al., J. Phys. Chem. C, 2017, 121, 15842–15850.

Fig. 1 Zwitterionic Gly–Pro. Reproduced with permission from the American Chemical Society. Copyright American Chemical Society 2016.

(34:[34]34) Philip Davies said: Please could you tell us what you calibrated your XPS to for both surfaces?

Vincent Humblot answered: For our XPS experiments, the calibration was carried out on the Au 4f 7/2 peak at 84.0 eV and on the Ag 3d 5/2 at 368.0 eV. Using such calibrations on our very thin □lms (thickness below 1 nm) ends up with the C 1s C–C, C–H position at 284.8 eV for all studied surfaces.

(35:[35]35) Philip Davies asked: I acknowledge the problems caused by the silver plasmon peak, but why does the signal-to-noise ratio in the N 1s region of Fig. 5 of your paper (DOI: 10.1039/C7FD00116A) get worse as the exposure time to the adsorbate increases? One would expect the opposite. Also in Fig. 5 of your paper, can you assign the low binding energy peak that develops in the N 1s region as the exposure increases?

Vincent Humblot replied: The N 1s data presented in Fig. 5 of our paper are the results of the substraction of the XPS signal before (Ag plasmon peak contribution only) and a□er adsorption of the dipeptide (contribution of Ag plasmon and nitrogen of the peptide). This substraction was weighted by the attenuation of the silver 3d signal, thus this induces some noise on the resulting peaks, especially

for the high coverage one. In the □gure shown here (Fig. 2), I present both raw and corrected XPS data. About the low energy peak appearing at higher coverage at 399.7 eV, the assignment is rather difficult taking into account both sets of data; it could well be an artefact due to the substraction of the Ag plasmon, or it could be due to the particular amide bond NH of the proline ring.

(36:[36]36) Han Zuilhof enquired: About four years ago we had a paper[1] predicting carbon 1s spectra from simple DFT calculations and Koopmans' theorem

Fig. 2 Raw and corrected N 1s region XPS data.

applied to core electrons. This yielded an average deviation of about 0.3 eV. We also extended this to N 1s calculations, yielding similarly small errors. Have you ever attempted something like this to help your assignment, either direct N 1s energy calculations, or to use the (more reliable) C 1s calculations to state something on the charge of adjacent N atoms?

1 M. Giesbers et al., Langmuir, 2013, 29, 4782.

Vincent Humblot responded: We haven't yet used DFT calculations to evaluate the splitting of XPS peaks within a given region. This is something we will certainly investigate in the near future. With the average deviation calculated of 0.3 eV, in the case of N 1s, with bands splitting between 1.3 and 2.0 eV, DFT calculations would unambiguously answer these questions.

(37:[37]37) Han Zuilhof commented: You are referring to energy differences between two N atoms of roughly 2 eV. This is clearly outside the error of the relative energies DFT calculations we've used, pointing to the potential of DFT calculations to sort out this unclarity.

(38:[38]38) Karl-Heinz Ernst said: I agree that in bulk samples or in thicker □lms of amino acids there are zwitterions, no doubt, but, again, experiments and calculations of aromatic N-containing molecules (e.g. quinoline) on gold show this N 1s peak at 402 eV, but no acidic group around. Lone pair electrons binding to the gold may show this peak as well. One should be more careful with just saying 402 eV is zwitterionic N 1s.

Vincent Humblot answered: Again, we agree with that experimental result on quinolone adsorbed on gold. However, as I stated in a previous answer, we are not assigning the 402 eV peak blindly to a NH_3^+ moiety, we support that assignment with the splitting observed between both contributions of the N 1s ranging between 1.2 and 2.0 eV. For more details, please see my answer to your earlier question.

(39:[39]39) Giovanni Costantini remarked: I imagine that if the dipeptide really becomes a zwitterion on the surface, then the picture is that it □rst adsorbs as a neutral molecule and stays neutral until it encounters another (neutral) molecule, and then the proton moves from one to the other. If this is what happens for Gly–Pro on Au(110), then you should see a clear signature for only neutral molecules at low coverage. Evidently, this is not the situation for your 10 min deposition. Have you tried to deposit much less? I think this would be a very important test to corroborate (or alternatively to disprove) the hypothesis that the molecules get in a zwitterionic state.

Vincent Humblot answered: We do believe that this is actually the phenomenon that is occurring at the surface, as our XPS data as a function of increasing coverage show an increase of the zwitterionic molecules at the surface between a 10 min dose and a 35 min dose, with the%of zwitterions going from 40 to 60%, approximately. However, we should indeed investigate lower dosing time to con□rm our hypothesis.

(40:[40]40) Giovanni Costantini commented: Assuming that Gly–Pro is zwitterionic on Au(110) at higher coverage, the relative intensities of the components in the C 1s and N 1s XPS spectra should be in a well-de□ned ratio. In the paper you give the "fraction of the O 1s contribution at higher BE (533.2 eV)", which, however, cannot be directly related to the NH_3^+/NH_2 ratio because the O signal also contains the HNC]O contribution. You should, however, be able to calculate the ratios between neutral, zwitterionic and anionic photoemission signals correctly (and independently) evaluated from the C 1s and N 1s spectra, and check that these are compatible. I think this would be a further essential test to corroborate (or alternatively to disprove) the hypothesis that the molecules get in a zwitterionic state on Au(110).

Vincent Humblot replied: We agree with you, and these calculations have been performed, even though they are only brie□y mentioned in the present paper. The

calculation method was applied to several of the systems we have investigated, and we can assume that our method is quite reliable. To answer more precisely to the question, we have found by cross-checking our data for N 1s, O 1s and C 1s that a□er a 10 min dose, the surface is covered with 40% of zwitterionic GP molecules and 60% of neutral GP molecules. The presence of anionic molecules was ruled out by the O 1s data. A□er 35 min of exposure, the calculations are more complex, and we end up with 65% of adsorbed molecules being zwitterionic and 35% of the GP molecules being either neutral or anionic. However, in this last case, our experimental data do not allow the differentiation between neutral and anionic molecules, and it is more than likely that DFT calculations suggested by Prof. Zuilhof could help us in deciphering this particular question.

(41:[41]41) Rasmita Raval said: Some very important issues have been raised regarding the structural determination of complex molecules at surfaces. My comment is that, □rst, such systems invariably need a multi-technique approach that pools data from spectroscopy, imaging, diffraction techniques and theoretical modelling. However, what is becoming increasingly clear is that the databases used to interpret the experimental techniques, e.g. vibrational frequencies and XPS binding energies, also need to advance. A good example is the number of years surface scientists took to understand how the vibrational frequency of CO at surfaces is affected by adsorption, the adsorption site and due to assembly as dipole and chemical shi□s come into play. As we make rapid progress in mapping complex molecule assemblies at surfaces, there is a need to understand how spectroscopic information from such systems can be interpreted correctly. This is a huge gap and represents a □eld of analytical science in its own right, and is crucial if we are going to advance towards knowledge-based design of functional surfaces.

Phil Woodruff communicated in reply: I completely agree. As you mention, there was a history of over-interpreting vibrational spectroscopy data in terms of structural assignments for the simple adsorbate CO and NO in the past, but there is clear evidence of similar things happening with scanning probe techniques and XPS for other molecules. Early in the history of surface science we learnt the need to apply several complementary methods to achieve a reliable understanding of adsorption systems, but in recent years this lesson seems to have been unlearnt. Both scanning probe microscopies and advances in DFT methods have played a huge positive role in understanding these problems, but are not sufficient in isolation. We need independent determination of surface composition, spectral □ngerprinting, and the application of quantitative structural methods to complement this information.

Vincent Humblot answered: We do agree with Prof. Raval; even using a huge number of techniques (experimental and computational) to investigate our systems (RAIRS, XPS, LEED, MS, NEXAFS, STM and MD, DFT) there are still gaps that need to be understood. We think that calculations on STM, RAIRS and XPS data (more and more present in the literature for the last 10 years) should help us increase our knowledge. Nevertheless, systematic experimental studies should still be carried out for fundamental knowledge to be increased.

(42:[42]42) Phil Woodruff addressed Vincent Humblot: The discussion of XPS core level shi□s in terms of only the initial state charge completely fails to take account of the □nal state relaxation effects. The fact that Prof. Ernst mentions DFT calculations showing a N 1s shi□ inconsistent with expected charge transfer is not surprising; on the contrary, it is entirely consistent with this view. Proper DFT calculations of core level shi□s account for both initial and □nal state effects. These core level shi□s are never a reliable guide to initial state charge transfer.

Vincent Humblot responded: We do agree with you that DFT calculations can be a real support when considering initial and □nal states relaxation effects; however, experimental results could never be occulted by theoretical calculations, and theoretical results should be confronted carefully with experimental data. Nevertheless, in the present paper we only take into account the □nal states and all our analyses are performed and compared to □nal states data, from us or from others.

(43:[43]43) Talat Rahman commented: I was also wondering, perhaps in your STM data, do you also □nd adatoms? There's a big difference between Au and Cu surfaces in their response to the peptides; could that be because in some cases you have more adatoms?

Vincent Humblot answered: We can never rule out the possibility of adatom

superstructures with these kinds of molecules. We have indeed evidenced the presence of adatoms with a slightly bigger molecule, a tripeptide Gly–Pro–Glu, which is binding on a chelating mode on Au surfaces and induces mass transportation.[1,2] In the present case of GP, we have not seen any evidence of adatoms on Cu(110) or Ag(110). However, on Au(110), we do not distinguish the (1 _ 2) reconstruction upon adsorption of GP, due to adlayer or to surface reconstruction? We cannot tell only with STM data; some complementary techniques would be needed (XRD, NEXAFS, etc.)

1 V. Humblot et al., J. Am. Chem. Soc., 2012, 134, 6579–6583.
2 V. Humblot et al., Surface Science, 2014, 628, 21–29.

(44:[44]44) Angelika K¨uhnle asked: Talking about zwitterionic species, I have three questions regarding the deprotonation of the carboxylic acid group. Firstly, you mention that the tendency to deprotonate is a function of the metal substrate, but it should also be a function of the speci□c molecule and its acidity. Is there a study addressing this point? Secondly, what happens in the gas phase? Are the molecules more prone to becoming zwitterionic in the gas phase than others? Finally, on the surface, where does the proton go?

Vincent Humblot responded: To our knowledge, there is yet no speci□c study addressing the peculiar point of the relation between the nature of the molecule vs. the nature of the surface adsorbing the given molecule when deprotonation/ dehydrogenation occurs. Some molecules do indeed have a tendency to be present as zwitterions either under a crystalline form or in the gas phase. This would probably in□uence the following adsorption and hence anchoring mode when this molecule arrives in the vicinity of a metal surface. In the case of Gly–Pro, as powder the molecule is neutral ($COOH/NH_2$) and so we believe it is also in the gas phase upon sublimation. We are currently trying to analyse the chemical nature of the molecular beam before the molecules land at the surface, but as you can imagine, it is tricky to implement. Finally, to where the proton goes a□er "deprotonation" of the carboxylic group, that remains a tricky point indeed. On the copper surface, protons are moving around until they □nd another for coupling and thus desorb as molecular H_2. That answers the case for anionic species, if one considers that Au and Ag will react accordingly to Cu surfaces. In the case of zwitterionic molecules, the answer could be simpler: the proton leaving the carboxylic acid ends up on the amine group that thus become protonated, and the charge equilibrium present in the molecular gas phase is maintained for adsorbed molecules.

(45:[45]45) Trolle Linderoth enquired: To follow up on the earlier comment from Giovanni Costantini which suggested that by going to low coverage one could isolate the neutral state of the molecule: Is it correct that the proton exchanges only occur on the surface? It could also occur, say, in the bulk state in the molecular evaporator?

Giovanni Costantini answered: I de□nitively think it is possible, actually I think that the starting material, the dipeptide powder, will probably be in the zwitterionic state (we have measured by XPS different dipeptide powders and found that this is generally true). However, I do not think that zwitterions would survive the sublimation. In fact, the very formation of a zwitterion in the solid (powder) state and on a surface is the result of the transfer of a proton from one molecule to a neighbouring one (possibly via the substrate for the on-surface case). So, when the molecules are separated (I guess it is safe to assume that what sublimes is individual molecules), I do not see how the zwitterionic state can be sustained.

David Amabilino communicated in response: It should be remembered that proton transfer could in principle be intramolecular, and does not necessarily take place between neighbouring molecules.

(46:[46]46) Angelika K¨uhnle said: I guess it is quite possible that the molecules form zwitterions in the sublimator. Whether or not they survive sublimation might again be a function of the speci□c molecule? When adsorbed on the surface, I could envision that also a single molecule can transform into a zwitterion, again depending on molecule and surface. My point is that the proton, being a positively-charged species, cannot leave the surface as neutral hydrogen. If it recombines to leave as hydrogen from the surface, it needs to get back the electron from somewhere. Can you comment on this process?

Vincent Humblot replied: I agree with you that the proton is becoming de facto a charged species and even when creating molecular H_2, it needs to recover an electron. The question can be reversed to the carboxylate group; what happens to

the delocalised electron once the oxygen atoms are “chemisorbed” at the surface? Is it possible that this same proton □nds its way to the H_3^+ radical lying nearby at the surface? Or is it more realistic/plausible that the metal surfaces act as a “sea of electrons”, thus providing the negative charge when needed?

(800:[47]47) Giovanni Costantini communicated: Molecular coverage is evidently an important parameter in your study. How did you compare the coverage across the three different techniques you used? Surely just using the exposure time cannot be a good way, because it is well known that the reproducibility of typical molecular sublimation sources used in surface science is rather poor, not to speak about the comparison between different sources in different UHV systems.

Vincent Humblot communicated in reply: This comment is correct, it is always very difficult to compare surface coverage by taking into account only the evaporation times. However, two of our techniques (XPS and RAIRS) are performed on the same UHV chamber with the same evaporation geometry, which limits the differences that can be observed. In addition, several identical experiments have been performed allowing us to estimate only a very small dispersion of coverage. As for STM experiments, carried out on a second and hence different experimental UHV, it is clear that identical evaporation time cannot be used as such. However, a calibration of the evaporation time was done by dosing small amounts of molecules until reaching full monolayer saturation. Again, several experiments were performed, allowing us to obtain quite a good correlation between dosing time used on both experimental setups.

(801:[48]48) Giovanni Costantini communicated: Because of the typical poor reproducibility of molecular sublimation sources, it would be better that for the XPS studies the actual coverage (evaluated by analysing the intensity of the core level signals) was quoted instead of the exposure time. Even if the absolute coverage values might still be questionable, at least relative values should be rather robust.

Vincent Humblot communicated in response: Again, we do agree with you and that is the reason why, in the present paper, for each coverage and for every surface (Ag and Au), as well as on a Cu surface,[1] the relative coverages in terms of monolayer (ML) fraction were calculated. For instance, on Au(110), a 10 min dose

corresponds to 40% of a saturated monolayer, while a□er 35 min, the relative coverage is close to 60% of a ML (page 4 of the manuscript, DOI: 10.1039/C7FD00116A). As for Ag, for dosing times of 10 and 35 min, we estimated the relative local coverages to be 35% and 60% of a monolayer, respectively (page 9 of the manuscript).

1 C. M´ethivier et al., J. Phys. Chem. C, 2016, 120, 27364–27368.

(802:[49]49) Giovanni Costantini communicated: How did you check that the Gly-Pro dipeptide is adsorbed intact and is not modi□ed/fragmented by thermal sublimation?

Vincent Humblot communicated in reply: During sublimation, the □ux of molecules was followed by mass spectrometry, showing no speci□c molecular fragments that could suggest a breaking of the molecule upon sublimation. Our sublimation power was very low (around 0.3 and 0.5 W) and should avoid any fragmentation of the molecules. In addition, XPS data were carefully analyzed showing a perfect stoichiometry for each C, N and O region, as well as all together.

(47:[50]50) Talat Rahman addressed Pol Besenius: In your paper, there was a detailed look at the system’s electronic structure, nature of bonding, etc. Are there simple models that you can point to, based on electronic structure calculations, that help one understand what’s going on in your systems? It would be nice to have simple models motivated by detailed calculations.

Pol Besenius responded: We are currently collaborating with a number of so□ matter physicists and theoreticians in the Netherlands and Germany to pursue both avenues, to help us in supporting structure formation in solution and on surfaces. One manuscript is currently in preparation and will be submitted in due course.

(100:[100]100) Phil Woodruff opened the discussion of the paper by Talat Rahman: I just want to return to a topic discussed in the previous session, namely core level shi□s in XPS. You do a full calculation of this adsorbate system and determine the charge transfer using a Bader analysis; whatever its imperfections might be, this is far more meaningful than any experiment can achieve. You then do a proper calculation of the XPS core level shi□ taking account of both initial

and □nal state effect. You then spoil this nice story by arguing that the core level shi□ that you determine is consistent with experimental values found in oxides with the metal atom in a known charge state and argue that this con□rms your calculated charge transfer. This is a non sequitur. You are nicely calculating the □nal state effect and then promptly ignoring it in making this comparison.
Talat Rahman responded: It was probably fortuitous that □nal state effects did not play a major role for the system on hand.
(101:[101]101) Steven Tait said: I would like to respond to the comment by Phil Woodruff about not being able to deduce charge state a priori from XPS. As Prof. Woodruff pointed out, we agree that the Pt 4f binding energy shi□ in the XPS data alone is not sufficient to prove a change in charge state of the metal centers, as there are other potential differences that could lead to a binding energy change, particularly a difference in □nal state effects. For this reason, multiple control studies were conducted to try to examine the binding energy changes.[1] We conducted XPS experiments on the same surface with Pt nanoparticles to examine the Pt(0) condition. We also tested that charge state by co-depositing Pt with a ligand that does not induce a charge transfer. We compare the Pt(II) state to a Ptporphyrin on the same surface as a second reference point. In later experiments,[2] we also veri□ed the complexation using high-resolution electron energy loss spectroscopy (HREELS).
1 D. Skomski et al., J. Am. Chem. Soc., 2014, 136, 9862.
2 C. G. Williams et al., J. Phys. Chem. C, 2017, 121, 13183–13190.
(102:[102]102) Phil Woodruff commented: If one sees the same chemical shi□s for a number of different systems, the implication is presumably that if the charge state is the same then the screening in the □nal state must also be closely similar. Strictly, you can't say anything about the separate initial and □nal state effects.
(103:[103]103) Steven Tait responded: Another important point regarding the on-surface redox activity of this system is that the system was designed to have a high likelihood of this type of reaction. The ligand used here, dipyridyltetrazine, is an excellent electron acceptor, and ligands similar to this are known to have a strong oxidizing ability as they coordinate metal atoms in nonsurface environments. Thus, it is not surprising that the charge transfer and redox reaction would be active, although this was the □rst report demonstrating that this reaction could be achieved in an on-surface environment with this type of ligand.[1]
1 D. Skomski et al., J. Am. Chem. Soc., 2014, 136, 9862.
(104:[104]104) Ioan Bˆaldea addressed Talat Rahman: You used Bader charge analysis to see charge transfer between adatoms. Have you also looked more microscopically at this charge transfer to see which orbitals are involved and changes in orbital occupations?
Talat Rahman replied: As you know, Bader charge analysis does not resolve the orbitals involved in charge transfer. It is an intuitive way to divide molecule or solid structures into atoms by de□ning zero-□ux surfaces that separate the atoms. We have not analyzed in detail the orbitals involved in the charge transfer. However, from preliminary charge difference plots (not included in the paper) we can see that in-plane components of Pt orbitals (d_{x2_y2}, d_{xy}) transfer electron to the pi orbitals of the tetrazine rings. Moreover, from Fig. 4b of the paper (DOI: 10.1039/C7FD00097A), based on the shapes of the depletion region (blue), we can conclude that the Au substrate has withdrawn charge from the pi orbital of the ligands and the d_{z2} orbital of the Pt atoms. The withdrawal from the d_{z2} orbital of the Pt atom is also evident by its shi□ closer to the Fermi level.
(106:[106]106) Markus Lackinger commented: The exact adsorption site of the Pt atom seems to be a crucial point. I was wondering if there is any experimental basis for this?
Talat Rahman answered: As we summarize in the ESI (DOI: 10.1039/C7FD00097A), we did try a good number of possible adsorption sites for Pt centers on Au(100) and found nine which were within 100 meV in total energy. We chose from this set the one with the lowest total energy. However, I should point out that we have not included entropic contributions which might also make a difference. At the moment we do not have experimental con□rmation of our calculated adsorption sites.
(107:[107]107) Steven Tait said: To respond to the previous question about the adsorption site: We do not have a precise experimental measurement of the adsorption site. The STM experiments were conducted at room temperature or at

higher temperatures. We have a precise measurement of the spacing along the chains, but not of the registry with the substrate. The spacing along the chains and the chain angle relative to the reconstruction rows of Au(100) indicate that the Pt atom sites would not all sit in the same adsorption site, but approximately every third Pt could be in the same adsorption site.[1] A virtually identical chain structure was observed using vanadium metal centers.[2] It is also interesting to note that although Pt nanoislands are able to li□ the surface reconstruction,[3] the Pt–DPTZ chains do not.

1 D. Skomski et al., J. Am. Chem. Soc., 2014, 136, 9862.
2 D. Skomski et al., J. Am. Chem. Soc., 2015, 137, 7898–7902.
3 C. D. Tempas, D. Skomski and S. L. Tait, Surface Science, 2016, 654, 33–38.

(108:[108]108) Trolle Linderoth addressed Talat Rahman: The structures were realised on hex-reconstructed Au(100). Would the situation have been different for the simpler situation of Au(111)?

Talat Rahman responded: Yes. On Au(111) we would not have found the corrugation that is present on Au(100) which accounted for homogeneity in the Au–Pt interactions in this system. Au(111) has the herringbone reconstruction, which might have added another type of complexity, but my hunch is that the Pt–Au interaction would have been weaker than in the present case.

(109:[109]109) Neil Robinson asked: From a heterogeneous catalysis point of view, you stress in the introduction of your paper the need to incorporate fewer precious metal atoms in the catalysts we design. However, you have then grown your metal–organic network on a gold surface. Not only do charge transfer effects between the active platinum sites and this gold surface render the structure relatively inactive (as alluded to towards the end of your paper), but such a system obviously involves a huge number of inactive precious metal atoms. Is it possible to form such a network on a less expensive surface, such as an industrially relevant oxide material, and do these structures provide evidence for enhanced catalytic activity?

Talat Rahman answered: Our work was motivated by the experiments of Tait et al. and hence the focus on Au(100) as the support for metal–organic structures. In a related theoretical study, we have compared the viability of a number of other metal atoms as the coordination center for the dipyridyl tetrazine network and found that several others (Mo, Cr, V, Fe and Co) may serve as a more active site for adsorption of molecules such as CO than what we have found for Pt. Of course, much computational work remains to be done before we can be con□dent in predicting that any one of these other metal atoms would serve as a more catalytically active site than what we have reported for Pt.

(111:[111]111) Steven Tait added: In response to the question about whether this has been tried on metal oxides: yes, we have attempted to grow these metal–organic chain structures on metal oxides. In fact, we have recently been conducting experiments to assemble metal–organic structures on high surface area oxide powders to explore their chemical and catalytic activity. We are preparing a manuscript now to report the □rst successful results from those experiments.

(112:[112]112) Deepak Dwivedi said: Thank you for the nice presentation. We know from the earlier studies that crystallographic morphology and surface energy of crystal faces have a great impact on the adsorption. I wanted to ask, could we characterize these aspects for a catalyst which has large surface heterogeneities? Is it possible to investigate these aspects under different operating conditions such as under different pressure and temperature? Can we calculate the effect of surface energy on the catalytic performance of a complex catalyst surface such as CNT or graphene etc.?

Talat Rahman answered: Your question has two important parts. The □rst is whether it is possible to characterize molecular adsorption characteristics for a surface with a large number of inhomogeneities such as steps, kinks, and terraces of □nite width. The answer is yes, if one knows a priori the nature of the inhomogeneity under experimental conditions. Alternatively, one could calculate adsorption characteristics for vicinal surfaces which have regularly patterned steps and kinks (represented by high Miller indices). Of course, these calculations require more computational resources than low Miller index surfaces. The other part of your question concerns calculations of adsorption characteristics under varying temperature and pressure. The answer to this is again in the affirmative, as one then calculates Gibbs free energy as a function of the chemical potential and temperature. You can □nd several examples of such calculations. One that comes quickly to my mind is in the calculations that we carried out for hydrogen adsorption on Co

nanoparticles as a function of pressure, temperature and coverage.[1] Here again, dealing with adsorption of a molecule such as dipyridyl-tetrazine (DPTZ) is going to be much more computationally intensive than hydrogen.

1 E. A. Lewis et al., J. Phys. Chem. C, 2012, 116, 25868.

(113:[113]113) Deepak Dwivedi asked: Just out of curiosity and for making my understanding clear, could you let me know whether you have observed the effect of crystallographic re-orientation on the catalyst performance (for example, gold or aluminum which has an FCC structure)? How easy or difficult is it to answer this question through □rst principle-based studies?

Talat Rahman answered: We have not carried out similar calculations for any other Au surface, neither have we looked at the adsorption of DPTZ on any other metal surface. We have con□ned ourselves to the reconstructed Au(100) since we were most interested in helping understand the experimental data obtained in Professor Tait's laboratory. We could extend these □rst principles calculations to the surfaces you mention. As we have shown in the present work, the charge transfer between the surface atoms and the Pt and ligand atoms plays an important role in determining the characteristics of the metal–organic network. I thus expect the results to depend on the nature (elemental, crystallographic) of the surface that we choose to study. It would be interesting to see the trends as a function of the nature of the substrate in future studies.

(114:[114]114) Karl-Heinz Ernst enquired: I'm interested in the activation of CO_2 activation and hydrogenation and in making it more efficient than today's energy-consumptive catalysts. We follow the same approach by testing metalcoordination compounds as potential catalysts, but as in your example, no activation is observed. What kind of metal would you put in a coordination compound in order to eject an electron into a CO_2 species for activation?

Talat Rahman responded: We have carried out calculations of CO_2 sequestration and also hydrogenation for a few novel catalysts, and the results have been gratifying as there is experimental evidence for the same. Interestingly, it is a metal-free catalyst, namely defect-laden hexagonal boron nitride (h-BN) that appears to be an appropriate one. The results of our initial joint experimental and theoretical work on hydrogenation of alkenes to alkanes are already in print.[1] We are in the process of submitting the results for CO_2 hydrogenation on h-BN.

1 D. J. Nash et al., ACS Omega, 2016, 1, 1343–1354.

(115:[115]115) Steven Tait opened a general discussion of the paper by Giovanni Costantini: There have been examples in the literature of ionic assemblies on copper surfaces that involve deprotonated carboxylic acid with cesium[1] or with sodium.[2] In those cases, the terephthalic acid deprotonates upon adsorption on the Cu surface and is, presumably, in an anionic state even before the alkali metal is deposited to the surface. In your case, do you think the charge transfer is occurring in a single step or does the TCNQ have a signi□cant amount of charge transfer before the complexation occurs? Does the TCNQ state change again when the potassium is deposited on the surface? What measurements do you think would be the most useful in examining this process in the future?

1 S. Stepanow et al., ACS Nano, 2010, 4, 1813–1820.

2 D. Skomski et al., J. Am. Chem. Soc., 2012, 134, 14165–14171.

Giovanni Costantini answered: TCNQ deposited on its own (i.e. without K) on Ag(111) forms metal–organic structures with Ag adatoms and is negatively charged. In this case, the charge is transferred from silver (from both adatoms and substrate). This system is described in Ref. 19 (in preparation) of our Faraday Discussions paper, DOI: 10.1039/C7FD00093F. In order to form the K-TCNQ metal–organic structures that are the subject of the present paper, K is deposited on top of the Ag-TCNQ phase and the sample is annealed to 470 K. This results in only slight changes in the SXPS spectra of TCNQ (C 1s and N 1s), while the K 2p SXP spectra are negatively shi□ed by 1.2 eV from K deposited alone on Ag(111), indicating that K gets positively charged.

(119:[119]119) Robert Jones said: The normal incidence X-ray standing wave data (NIXSW) was taken using the (111) Bragg re□ection and provides positions for the various molecular components along the surface normal, relative to the (111) Bragg planes. Reciprocal space data indicated that the ad-layer was incommensurate with the gold substrate. As stated in the paper (DOI: 10.1039/C7FD00093F), this means that (for a rigid ad-layer) all positions determined by NIXSW relative to planes at an angle to the surface normal, such as (_111) re□ections, should give a coherent fraction of zero; i.e., all adatoms are at all possible positions relative to the angled Bragg planes. Were any NIXSW data

obtained using such angled planes, and did they show the expected zero coherent fraction? Would the authors care to speculate whether it is possible that an overlayer comprising a complex molecule with some □exibility, such as here, could be incommensurate overall, but with some of the more strongly bonding entities (e.g. N in CN) pulled into higher symmetry sites such that they are partially ordered relative to the substrate? If this were the case, then (_111) NIXSW may show a non-zero coherent fraction.
Phil Woodruff responded: Because the overlayer was known to be incommensurate, no triangulation measurements of the (_111) NIXSW were made. It is perfectly true, of course, that even in an incommensurate molecular overlayer there could be local distortions of the molecule such that, in the case of TCNQ for example, the N atoms that bond to the Ag surface may try to adopt slightly more favourable local sites. However, with four N atoms per molecule in symmetrically inequivalent sites relative to the substrate, none of which are likely to lie very close to high-symmetry local adsorption sites, the (_111) coherent fraction (averaged over all symmetrically-equivalent azimuthal rotations and the many inequivalently located molecules in the surface unit mesh) can be expected to be very low even if local distortions do occur. In this situation it is difficult to see that the information gained would really be interpretable in terms of a speci□c structural model.
(120:[120]120) Phil Woodruff commented: It's perhaps worth stressing that a LEED pattern provides valuable complementary information to STM in understanding the long-range order. Of course, in STM it's easy to measure the approximate size of the unit mesh of an ordered surface phase, but unless it's also possible to image clean areas of the surface at the same time it's very difficult to make a reliable assignment as to whether this phase is commensurate or incommensurate because of problems of dri□ and/or piezo calibration. By contrast, LEED always shows the substrate diffraction and the overlayer diffraction and the exact relationship of the two can be established.

(121:[121]121) David Amabilino asked: Regarding Fig. 1b in your article (DOI: 10.1039/C7FD00093F), the nice pattern you see and assign to the K ions on top: when you look at the TCNQ image, that looks extremely well ordered, but when you look at the K image, the domains look a lot smaller (less well ordered?) and there are differences in contrast. Could that be re□ecting the different directions of the cyano groups or what is that re□ecting?
Giovanni Costantini responded: At the speci□c scanning conditions (tip state and negative bias voltage) shown in Fig. 1b of the article, K atoms are appearing as bright protrusions. The apparent lower order in Fig. 1b is thus most probably the result of the absence of K atoms in some of the windmill structures within the network. We checked this by intentionally reducing the K exposure, which results in a higher number of K vacancies (see ESI Fig. S3).
(122:[122]122) David Amabilino said: So what you're saying is the irregularity is because there is no K ion there? It seems that even in the ordered domains of the potassium cation there is some irregularity; did you look at the contour line along rows of atoms to see if there was variance, possibly because of the cyano group orientation?
Giovanni Costantini responded: Yes, the irregularity is not in the TCNQ molecules, these are still ordered in a regular interdigitated windmill network (please note that the TCNQmolecules can still be seen in Fig. 1b of the paper but are less apparent because of the higher apparent height of the K ions). The irregularity is given by the fact that some of the K ions are missing, and in the imaging mode shown in Fig. 1b the K atoms are more evident. I guess that the "irregularity" you refer to that should exist "even in the ordered domains of the potassium cation" is related to the STM apparent height and not to the lateral position (which seems to be quite regular tome). It is true that not all the K ions appear to have the same height, but this is actually also true for the TCNQ molecules as seen under the imaging conditions displayed in Fig. 1a. We have no idea about the origin of this slight contrast difference and we have not examined this in detail. Interpreting the measured height of STM images is however quite tricky, as one needs to have a full knowledge of the metal–organic interface and of the tip. We can, for example, not exclude that the incommensurability between the molecular adlayer and the Ag(111) substrate could play a role. However, we would exclude that the different apparent height of some of the K ions is caused by the fact that these are corresponding to (a majority of)

those cyano groups that have a speci□c orientation. In fact, if this was true, one would expect that there existed (at least) two different K adsorption sites, while the coherent fractions determined from our NIXSW measurements indicate a single adsorption site.

(123:[123]123) Rasmita Raval enquired: Given that the system is incommensurate and does not adopt speci□c adsorption sites at the surface, would you expect to see a range of N environments and heights in your system? A number of N environments and heights may also arise from molecules that are not imaged, e.g. within the disordered 'sea' surrounding the ordered domains. In addition, these molecules are likely to have signi□cant mobility, regardless of charge. A□er all, the charged molecules in your system self-assemble, which implies mobility across the surface. Would these lead to the low coherent fractions seen in the N 1s NIXSW?

Giovanni Costantini replied: To the □rst question: "The fact that the metal–organic superstructure is incommensurate with the substrate implies a range of N environments and heights". The fact that TCNQ molecules have several nonequivalent adsorption sites will surely add to the reduction of the coherent fraction f. However, we think that this will be a secondary effect. The presence of K vacancies (for which we have experimental evidence) is expected to contribute more to reduction of f. However, as discussed in the paper, even the presence of K vacancies is not enough to account for the measured low value of f. The model we propose in the paper is the simplest we can think of that explains the experimental data. To your second question: "Mobile molecules that are not imaged in the STM data could lead to the low coherent fractions seen in the N 1s NIXSW". The NIXSW measurements were always performed on systems prepared in full monolayer conditions for which the number of mobile molecules can be expected to be extremely small.

(126:[126]126) Phil Woodruff commented: As I understand it, Prof. Raval is suggesting that molecules in disordered regions or where the molecules are mobile could account for the low coherent fractions seen in the N 1s NIXSW. However, it's notable that the C 1s NIXSW shows a high coherent fraction, so the implication is that there is no signi□cant variation in the heights of the molecules above the surface. Notice that the coherent fractions for these (111) re□ections are a measure of the 'order' in the heights of the constituent atoms, and it's hard to see why lateral disorder of these large molecules should have much effect on this. As the standing wave technique is not widely known, it's perhaps worth commenting on the proper interpretation of the coherent fraction. It is generally thought of as an order parameter, and it is certainly true that disorder (e.g. thermal vibrations) does lower the coherent fraction. However, it's also true that if a system is perfectly ordered but has two equally-occupied atomic sites that differ in height by exactly half the substrate interlayer spacing, then the coherent fraction is exactly zero.

(127:[127]127) Steven Tait asked: Following on from the comment by Rasmita Raval about diffusion of molecules across the surface, the high diffusivity of this system is interesting. There are examples of organic adsorbates with high diffusivity, including some where increasing the size of the adsorbate leads to a signi□cant increase in diffusivity due to a mismatch of binding units in the molecule with the spacing of the surface atoms.[1] In this case, it seems that the diffusivity is high, even a□er the deposition of potassium on the surface. Would it be reasonable to consider units of $K^+(TCNQ^-)$ diffusing across the surface as a zwitterionic complex?

1 D. Skomski and S. L. Tait, J. Phys. Chem. C, 2013, 117, 2959–2965.

Giovanni Costantini answered: It might be the case, but unfortunately we do not have any evidence or measurement regarding the diffusion of TCNQ molecules or TCNQ-K or, another possibility, TCNQ-Ag complexes.

(128:[128]128) David Amabilino enquired: As a follow-up on my previous question and relating to the point about the nitrogen position, if your coverage of K is not 100%, can you see the difference between a TCNQ in proximity to the silver substrate and a charged TCNQ modi□ed by the presence of the potassium cation by that technique? How sure can you be that your different contributions from the standing wave technique are not coming from different charged species, one closer to the surface, the other slightly pulled up to the potassium cation?

Giovanni Costantini responded: I agree that part of the N low coherent fraction measured by NIXSW might (actually will) be due to the presence of K vacancies. But, as we demonstrate in the paper (DOI: 10.1039/C7FD00093F), the measured

density of defects (around 20%) is not enough to explain the measured low coherent fraction.
(129:[129]129) Rasmita Raval asked: Were image charges accounted for in the description of charged molecular systems at surfaces?
Giovanni Costantini replied: We clearly expect that the highly polarizable metallic substrate will tend to screen localized charges on both the TCNQ molecules and the K ions. In fact, in the paper (DOI: 10.1039/C7FD00093F) we write: "The high electron affinity of TCNQ molecules means that they become charged on metallic substrates, and the combination of the charged molecules and their image charges in the metallic substrate creates relatively strong dipole moments perpendicular to the surface. The mutual repulsion of these dipoles might be expected to suppress self-assembly, but the addition of metallic adatoms – in particular alkali adatoms – produces strong dipoles of opposite polarity, stabilising the metal–organic networks, and also reducing the work function increase caused by the negatively charged TCNQ molecules in isolation."
(131:[131]131) Lifeng Chi opened the discussion of the paper by Nian Lin: We have a quite similar system but with hydrogen bonding. The structures are formed by 2-fold and 3-fold hydrogen bonding, strongly coverage dependent. But in our case, they did not mix together.
Nian Lin responded: Interesting. This phenomenon shall be very general, not limited to metal–organic systems.
(132:[132]132) Lifeng Chi asked: How many coordination bonds can the Cu atom form?
Nian Lin responded: Two or three.
(133:[133]133) Lifeng Chi enquired: The spectroscopy you did, was that on molecules or on coordinated Cu atoms? If it was on molecules, can you see the difference in HOMO–LUMO with the 2-fold and 3-fold coordination?
Nian Lin responded: The STS data were acquired on both the molecules and Cu atoms. We cannot conclusively determine HOMO or LUMO in STS. DFTcalculated PDOS might be useful for us to assign the STS features to HOMO/LUMO.
(134:[134]134) Trolle Linderoth said: In a recent paper[1] we showed that surface MOCNs can involve Cu-trimers rather than single adatoms at the interaction nodes. Could Cu-trimers be responsible for the three-fold coordination nodes you observe, and help to explain why both two-fold and three-fold coordination nodes are observed in the network ?
1 F. Bebensee et al., Angew. Chem. Int. Ed., 2014, 53, 12955–12959.
Nian Lin replied: The distance between neighboring pyridyl ligands, as determined by the STM image and molecular modelling, is too short to accommodate three Cu adatoms. A single Cu adatom coordinated by three pyridyl units in a three-fold motif renders a Cu–N distance of about 2.1 °A.
(135:[135]135) Giovanni Costantini remarked: The ext-TPyB molecule has 3-fold symmetry and shows both 2-fold and 3-fold coordination. I do not think that the extremely high degree of regularity, the high porosity, and the extension of the observed metal–organic networks it forms in the D-phase are compatible with a random "choice" of the Cu ions in the network to coordinate either two or three pyridyl groups. I rather think there must be some type of energetic gain, such that if one of the pyridyl groups of an ext-TPyB molecule is already involved in a 3-fold coordination node, the chances of the two remaining pyridyl groups of the same molecule to be also involved in a 3-fold coordination node are essentially zero. Is there any evidence for this? Do you have plans to look deeper into this possibility?
Nian Lin replied: This is an interesting thought. I do not know any physical/chemical mechanism that can cause the coordination of one terminal group to affect those of others that are located quite some distance apart. It's worthwhile to search the literature or ask chemist colleagues to see if such phenomena are known in chemistry. Experimentally, we can examine the behavior of normal TPyB. If your proposed mechanism is at work, it shall be expressed also in TPyB.
(137:[137]137) Talat Rahman asked: Could your structures also be driven by the strain in the system? The underlying substrate could be playing a role.
Nian Lin replied: Yes, we believe the structure is driven by an in-plane compression due to high molecular coverage. Yes, all Cu atoms in the structure are sitting at the Cu(111) lattice epitaxially.
(138:[138]138) Trolle Linderoth remarked: In relation to the question of the mechanism behind formation of your metal–organic coordination networks: Your STM images show the perfect extended structures. Can information on the growth mechanism and underlying interactions be inferred from images during early

stages of growth or from defects/edge terminations?
Nian Lin answered: To follow the growth process will provide insights into the formation mechanism. Experimentally, however, this is not so easy using STM. LEEM might be an ideal technique.
(140:[140]140) Talat Rahman said: I am very glad to see you attain networks with several different symmetries at the metal coordination center. This is something that my colleague Ludwig Bartels and I were trying to look for, motivated by our □ndings of pattern formation of arenethiol □lms on Cu(111),[1] but have not succeeded so far.
1 K.-Y. Kwon et al., J. Am. Chem. Soc., 2009, 131, 5540–5545.
Nian Lin responded: I am very much looking forward to the deep insights of this structure being revealed by theory. I can send you our data if you are interested.
(142:[142]142) Talat Rahman enquired: You did have some coverage dependence?
Nian Lin responded: Yes, as shown in Fig. 3 of our paper (DOI: 10.1039/C7FD00088J).
(144:[144]144) Talat Rahman asked: I think the question is whether the coordination is taking place □rst locally and then progressing gradually, or that the ordering takes place all of a sudden for a particular coverage?
Nian Lin replied: Very important question. Since experimentally STS does not see the "real" growth, but the static structures formed a□er annealing, we cannot answer this question. LEEM or kMC might be able to shed some light.
(145:[145]145) Steven Tait said: In the structure that you found to be thermodynamically stable (D-phase), there are a signi□cant number of three-fold coordination sites of pyridyl around Cu atoms. In prior studies of pyridyl–Cu coordination on surfaces, the two-fold motif is usually seen,[1,2] but not the threefold. Can you comment on why the three-fold coordination structure is not typically seen in surface studies of Cu coordination to pyridyl groups, but was observed here?
1 Y. Li et al., J. Am. Chem. Soc., 2012, 134, 6401–6408.
2 S. L. Tait et al., J. Phys. Chem. C, 2007, 111, 10982–10987.
Nian Lin replied: You are right that two-fold coordination is energetically more favored than three-fold. At the coverage of forming D-phase, however, a structure consisting exclusively of two-fold coordination would be under huge in-plane compression. I speculate that this compression shi□s the free energy landscape since the structure with three-fold coordination occupies less space.
(147:[147]147) Steven Tait asked: To follow up on my previous question, would you please comment on how the surface structure differs post-annealing between low coverage and high coverage?
Nian Lin answered: The structures shown in the paper are all a□er annealing. So they are thermodynamically equilibrium structures at the speci□c coverage.
(148:[148]148) Talat Rahman commented: I worked with arenethiol molecules on Cu(111) some time ago. We found these 3-fold structures in STM images taken by Ludwig Bartels' group. We found in our calculations that it was arising from Cu adatoms.[1]
1 K.-Y. Kwon et al., J. Am. Chem. Soc., 2009, 131, 5540–5545.
Nian Lin responded: Very interesting.
(149:[149]149) Marco Sacchi asked: Do you think you could observe similar self-assembly structures on other metal surfaces?
Nian Lin replied: In principle, yes, as far as a metal can coordinate with a ligand in two- and three-fold coordination simultaneously.
(150:[150]150) Marco Sacchi said: There are other metals that could coordinate either two or three ligands, for instance iron.
Nian Lin answered: To my knowledge, iron can be of three- or two-fold coordination with different ligands. Recently, we indeed found that Eu can coordinate with CN in 2-, 3-, 4-, 5- and 6-fold coordination, which leads to a quasicrystalline network.
(151:[151]151) Steven Tait enquired: How do you account for the striking difference in the scanning tunnelling spectroscopy measurements on the two-fold vs. three-fold Cu centers? Does that agree with expectations of the electronic states based on what is known from other metal–organic systems (including those not at surfaces)?
Nian Lin responded: We need theory (DFT) to answer this question. PDOS shall be able to tell the difference.

(152:[152]152) Peter Beton said: You have one defect in one of your images, is that a missing molecule? I was interested in what sort of defects you do see, and also, what you see at the domain boundaries. You've got this different coordination, when you see these ordered structures you'd expect to see some faceted edges. What kind of facet would you expect to see at the edges of this kind of island?
Nian Lin replied: The defect is not a missing molecule, but three molecules that coordinate to a central Cu atom undergo a 60_ rotation around the central Cu. We saw domain boundaries when the molecular coverage is below or above the perfect coverage of forming the D-phase. In the D-phase, each 3-fold coordination is surrounded by six 2-fold coordinations and each 2-fold coordination is surrounded by three 2-fold and one 3-fold coordinations. What happens at the domain boundaries is the 2-fold and 3-fold coordination motifs are not perfectly arranged in such a manner. The edges of the D-phase always are boundaries since this phase is formed when the entire surface is covered by the molecular networks. The domain boundaries are not straight and o□en irregular, so it's not clear what facets they are.
(153:[153]153) Peter Beton asked: Can the phases grow continuously into one another? Can the hexagonal network grow continuously on an edge of this demiregular network without any obvious boundaries?
Nian Lin answered: Experimentally we cannot see the real "growth". So, even though experimentally we did adjust the coverage gradually, what we "see" is the structures formed a□er annealing the sample at each coverage, which does not represent "continuous growth". This is the limit of STM. LEEM could be an ideal tool to answer your question.
(155:[155]155) Brandon Hirsch enquired: Prof. Lin, my question pertains to probing the kinetic pathways involved in the phase transition from the demiregular lattice with a combination of 2- and 3-fold Cu centres to the S phase with exclusively 3-fold Cu centres. What would you expect if you formed a full monolayer of the demi-regular lattice, then added more of the ligand without annealing and analysed it structurally with STM? In principle, the molecules would coordinate at the 2-fold sites to form 3-fold Cu centres, but this would simultaneously close off the neighbouring pores.
Nian Lin replied: Very good suggestion. We have not done that, but it is de□nitely worthwhile to try it.
(156:[156]156) Rasmita Raval commented: Are the pore size and patterns observed in your surface tilings similar to those seen in zeolites and MOFs? Can you comment on the possibility of creating very different patterns and pores in a surface 2D system, which would lead to different functions compared to 3D porous materials?
Nian Lin responded: Yes and no. The underlying chemistry and assembly mechanism of the 2D porous structures are very similar to the MOFs. However, in zeolites and MOFs, there are pores for channels and compartments that can transport or store molecules. The 2D porous structure does not have such functions. In 2D systems, guest molecules are con□ned in 2D compartments. The reduced freedom might be exploited for stereo-selective reactions. In addition, one unique feature of the 2D systems is that the metal centers in these structures are unsaturated and easily accessible, which may be useful in heterogeneous catalysis.
(158:[158]158) Talat Rahman said: It would be a good idea to do it on another surface that does not interact strongly with the molecules. Just to see if it's a strain and geometric effect, or if it's really electronically driven –that would be nice to know.
Nian Lin answered: To distinguish the two effects, we need an inert surface. BN might be a choice. We will look into it.
(159:[159]159) Trolle Linderoth opened a general discussion of the topics raised at the session: Turning to the more general discussion of characterisation of metal–organic coordination networks, the NIXSW technique used to determine the adsorption height of K-atoms in the K-TCNQ network is very elegant. Could it be employed for the other networks we have discussed in this session? In particular, would it be applicable to the hex-reconstructed Au(100) surface where the topmost hexagonal Au layer breaks the periodicity of the underlying bulk structure which sets up the X-ray standing wave pattern?
Nian Lin answered: De□nitely. In particular, to determine the height of metal adatoms is extremely important.

Giovanni Costantini replied: The answer to the □rst, more general, question is yes, the NIXSW technique can (and indeed I think it should) be used for other molecular structures at surfaces, including some of those presented in this session. The NIXSW technique is not “disrupted” by a reconstructed surface, in the sense that the wavelength of the standing wave would still be that of the bulk interlayer spacing, irrespectively of a reconstructed surface. However, the NIXSW technique only tells about the height of an atom above the scattering planes of the chosen Bragg re□ection which, in the case of a reconstructed surface, do not coincide with the outermost atomic layer of the surface. As such, it would be more difficult to determine surface–molecule bond lengths for a molecule adsorbed on a reconstructed surface.

(160:[160]160) Phil Woodruff commented: The standing wave is established in many layers of the substrate over a thickness of _microns, so a reconstruction of the outermost layer or layers has no effect on the viability of the technique. However, what one measures is the height of an absorbing atom relative to the nearest extended bulk layer, not relative to the nearest actual layer, so surface reconstruction or relaxation means it is not trivial to relate the NIXSW height to adsorbate–substrate bond lengths. If the atoms in a reconstructed layer had sufficiently large surface core level shi□s relative to the bulk then NIXSW could be used to measure this effect, but in practice this never seems to be the case.

(165:[165]165) Phil Woodruff said: The issue of how to deal with systems for which DFT calculations indicate several structures have very similar total energies is one we have recently had to address in a study of TCNQ (without coadsorbed alkali atoms) on Ag(111) and is presented in the poster by Phil Blowey. The ordered phase studied is commensurate with three molecules per unit mesh, and the combination of our NIXWS results and those of DFT calculations is that Ag adatoms are also involved in this phase, but the question is whether there are one, two or three adatoms per unit mesh. DFT calculations show two possible models, in particular, to have very similar energies that are signi□cantly lower than most of the other structures. We have therefore compared our experimental structure parameter values with those based on a model in which the different possible structures are assumed to be co-occupied with probabilities given by the appropriate Boltzmann factors. This seems to lead to good agreement. Notice, though, that this treatment does not include entropic effects.

(166:[166]166) Giovanni Costantini said: I have a general comment on the need for experimental quantitative structural characterisation of surface-based molecular structures. The great majority of the work in this area available in the literature is based on a combination of STM and (typically) DFT-based calculations. While STM is an invaluable tool for determining the lateral arrangement and periodicity of a supramolecular structure and sometimes can also give information on the orientation of individual molecules, it cannot determine the actual structure of the molecule–substrate interface (i.e. the height and lateral position of the atoms constituting the molecule with respect to the substrate atoms), or (very o□en) determine whether the molecular superstructure is commensurate with the substrate or not. In most of the literature available in the □eld, the only quantitative structural information on an adsorbed molecular structure is that which is obtained directly from theory. This is particularly dangerous (unreliable) if the simulation needs to be done within a cell with periodic boundary conditions and if the simulation cell is chosen based only on the STM results. To properly resolve and understand a molecule–substrate structure, independent, experimental, quantitative structural determination is essential. Unfortunately this is not what is typically done, but the good news is that a number of techniques are available, such as NIXSW and LEED I–V. Performing and interpreting these experiments might not always be easy and straightforward, but it is de□nitively needed if a proper understanding of these systems is what we are looking for. Moreover, high quality experimental quantitative structural determination is the best way to benchmark DFT calculations, which is essential when dispersive interactions are included.

Phil Woodruff replied: I certainly echo these comments. The combination of STM and DFT alone is not a reliable way of determining surface structures. One problem is certainly the issue of the reliability of the atomic coordinates determined by DFT, particularly in systems where van der Waals interactions are important and the choice of the appropriate dispersion-corrected version of DFT is not clear. Quantitative structural information can provide valuable benchmark data to help to address this problem. In addition, however, it’s important to

remember that DFT, like quantitative experimental surface structural methods, can only □nd the correct structure if the initial structural model is correct. STM images can certainly be helpful in trying to identify possible structural models, but are not a substitute for more quantitative experimental structural data.
Talat Rahman responded: One should also note that most DFT calculations of STM images are also based on approximations and do not take into account the nature of the tip, which may have an impact on what is being imaged. The good news is that computational codes that employ more realistic DFT calculations are now emerging.
(167:[167]167) Talat Rahman commented: There was a time when we were getting a lot of vibrational information about systems, STS measurements, vibrational spectroscopy, providing a lot more information. We can't rely solely on DFT or any one structural method.
(168:[168]168) Marco Sacchi said: I strongly agree with what you are saying. We have been measuring benzene dynamics and comparing HeSE results with DFT calculations. It is remarkable that, as far as I know, there is still not a very accurate height measurement for such an important molecule, but just an indirectly deduced value. Indeed, as a theoretician, I would like to have this kind of quantitative measurements of structural parameters, since they are essential in order to benchmark dispersion-corrected DFT schemes, for instance.
Phil Woodruff replied: There are quite a number of fully quantitative experimental structure determinations for benzene on various surfaces. These include our own determinations of the local structure of benzene at low coverage (no longrange order) on Ni(111) and Ni(110) and an ordered phase on Ni(111).[1,2] There are also a number of structure determinations using quantitative LEED, initially from the Somorjai group starting in the 1980s, on Co, Pd, Pt and Ru surfaces.
1 O. Schaff et al., Surf. Sci., 1996, 348, 89.
2 J.-H. Kang et al., Surf. Sci., 2000, 448, 23.
Talat Rahman responded: There are some relatively old experimental data (LEED) for benzene on Pt. See, for example, ref. 1. But you are right that the experimental value of the height of benzene over other metals is not readily available.
1 A. Wander et al., Surf. Sci., 1991, 249, 21.
(170:[170]170) Trolle Linderoth commented: Our interesting discussion of metal–organic coordination networks has shown that further understanding of the metal–ligand interaction nodes (symmetries, binding energies) as well as the nucleation mechanism of the networks are very interesting questions for future studies. Are there other questions that the community sees as particularly relevant to address?
(171:[171]171) Talat Rahman said: I think we are fortunate that with the foundation laid over four decades by surface science and with a plethora of recent advances, we are getting a lot of information, so much data is available from experiments and computational modelling. This is great as these provide good tests for theoretical models. We also recognize that future advances in DFT need to include considerations of dynamics and kinetics. It is □ne to use structures obtained from DFT as the starting point, but we have to understand and accept the limits of DFT. It is, a□er all, a technique for determining the system's ground state at zero temperature. We should encourage those looking at many other factors affecting ordering at surfaces, including coverage dependence, kinetics, vibrational entropy, etc.
(172:[172]172) Nian Lin remarked: Self-assembly, by its nature, is a dynamic process. However, so far we primarily use STM and DFT to study the static states. We need some new tools to resolve the dynamics, for example, molecular dynamics and fast XPS.
(173:[173]173) Talat Rahman commented: One more thing I wanted to add, which I alluded to earlier, is that while there is the need to continue to develop more accurate and robust methods beyond DFT, which can describe reliably the properties of nanostructures in complex environments, out-of-equilibrium and nonadiabatic, there is also the need to build some simple models that explain the behaviour of complex molecules as shown in so many nice presentations here. With the information from DFT, one could use, for example, coarse graining and related methods from statistical mechanics to understand how peptides order on surfaces, whether they form dimers or other structures. It is important that our theory and modelling in concert with experimental data tells us something about the nature of the interactions responsible for complex molecular ordering on surfaces on a global, general level, as not everyone can or should perform these expensive DFT calculations for all systems. Nature is inherently simple, and

physical reasoning allows us to break complex structures into simple parts for better understanding. I believe more efforts along such directions would be good.